Microbial dechlorination of polychlorinated biphenyls, dibenzo-p-dioxins, and -furans in groundwater at the Portland Harbor superfund site, Oregon, USA

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ABSTRACT

The Portland Harbor (Oregon, USA) has been declared a 'Superfund' site because it is impacted by a variety of contaminants, including polychlorinated biphenyls (PCBs) and polychlorinated dibenzo-p-dioxins and –furans (PCDD/Fs). PCBs and PCDD/Fs are persistent organic pollutants that generally do not degrade in most environments. One of the few pathways for their transformation is dechlorination by anaerobic bacteria. This process has long been known to occur in sediments. Recently, it has been recognized that PCB and PCDD/F dechlorination may also occur in other anaerobic environments, such as in landfills, sewers, and groundwater. In this work, data on concentrations of PCBs and PCDD/Fs in sediment and surface water were analyzed using Positive Matrix Factorization (PMF). The results indicate that a factor related to the dechlorination of PCBs and PCDD/Fs was present in the surface water but not in the sediment. Groundwater flow into the Harbor is rapid, and the spatial patterns in dechlorination products suggest that they come primarily from groundwater and possibly also from the combined sewers that service this area. Dechlorination products comprise 22% of the PCBs in the water column, suggesting that dechlorination is more extensive in the Portland Harbor than in the Delaware River, but not as extensive as in the Hudson River (New York/New Jersey Harbor), which is well-known for extensive microbial dechlorination in the sediment. The Portland Harbor therefore represents the third major US watershed in which PCBs appear to undergo dechlorination in an environment other than sediment, suggesting that the microbial dechlorination of PCBs and PCDD/Fs is more common than

previously assumed. In addition, the Portland Harbor is impacted by PCBs generated inadvertently during the production of pigments. The median concentration of PCB 11 from pigments was 22 pg/L in 120 whole-water samples from the Portland Harbor, and in two samples, PCB 11 alone exceeded the 64 pg/L federal water quality standard for the sum of PCBs.

INTRODUCTION

The Portland Harbor (Oregon, USA) is similar to most of the major harbors of the US in that it is heavily impacted by a variety of contaminants arising from local industry and urbanization, with persistent organic pollutants such as polychlorinated biphenyls (PCBs) and polychlorinated dibenzo-p-dioxins and –furans (PCDD/Fs) being some of the main contaminants.[1] There are over 60 facilities on the harbor that may be sources of contamination.[1] The harbor from river mile (RM) 1.9 to 11.8 was placed on the National Priorities List (i.e. 'Superfund') in 2000, triggering a large data collection effort. (RM 0 is defined as the confluence of the Willamette and Columbia rivers.)

In such a complicated system, source apportionment can be a useful tool to elucidate the main sources of contaminants such as PCBs.[2-4] In addition, source apportionment via factor analysis can identify important processes, including natural attenuation, which might be occurring.[5, 6] PCBs and PCDD/Fs are recalcitrant compounds that generally do not degrade in most environments. For PCB and PCDD/F congeners with more than two chlorine substituents, one of the few pathways for their degradation is dechlorination by anaerobic bacteria, which use the chlorinated compound as an electron acceptor for respiration (dehalorespiration),[7] removing some chlorines while leaving the biphenyl backbone intact. This process is important in the Hudson River, another superfund site where high levels of PCBs in the river sediment have led to extensive microbial dechlorination.[8] Recently, it has been recognized that microbial dechlorination of PCBs and PCDD/Fs may occur in other anaerobic environments, such as landfills, sewers, and groundwater.[9, 10]

The purpose of this study was to examine the data on PCB and PCDD/F concentrations in surface water and sediment at the Portland Harbor superfund site in order to identify sources and degradation processes. A second purpose was to compare the sources/processes for PCBs and PCDD/Fs with those observed in two other systems for which a large amount of high quality data is available: the New York/New Jersey Harbor (and associated Hudson River) and the Delaware River. Data for the NY/NJ Harbor are taken from the Contamination Assessment and Reduction Project (CARP),[6, 11] and data for

the Delaware River were collected as part of the effort to establish a Total Maximum Daily Load for PCBs.[9, 12, 13]

METHODS

Portland Harbor is a tidal estuary that is home to the city of Portland, Oregon, with a population of about 600,000 (see map, supporting information figure S-1). Water and sediment samples were collected during 2004-2007 under a series of EPA-approved quality assurance project plans. Water sampling campaigns were designed to capture low flow (November 2004; March and July 2005; September 2006), high flow (January 2006, January through March 2007), and 'stormwater influenced' flow (November 2006). Figure S-2 of supporting information shows the locations of water sampling. Details of sample collection are provided in the quality assurance project plans.[14-16] This and other technical documents related to the site are available at: http://yosemite.epa.gov/R10/CLEANUP.NSF/ph/Technical+Documents. Briefly, surface sediment and beach sediment samples were collected with either a handheld coring device (subaerial beaches), small dredge sampler (shallow water beaches), or power grab sampler (river channel and river nearshore areas), and sediment cores were collected with a vibracoring device. Sediment samples were analyzed for PCB and PCDD/Fs (and many other contaminants not discussed here) as well as total organic carbon. Water samples (about 400 L each) were collected using an Infiltrex 300 pump system (Axys Analytical Services). Particles were retained on a 0.5-µm glass fiber filter. Dissolved phase contaminants were collected on a column of XAD-2 resin. All 209 PCB congeners were measured using EPA method 1668 (revision not specified), and the 17 2,3,7,8-substituted PCDD/Fs were measured via EPA method 1614.

Data on concentrations of PCBs and PCDD/Fs in surface water and sediment at the Portland Harbor superfund site were obtained primarily via the EPA's STORET database (http://www.epa.gov/storet/). Although the Remedial Investigation (RI) Microsoft Access database was also consulted (provided as Appendix F of ref [1]), STORET contained more data (more samples) for PCBs in the water column than the RI database. The data was checked to ensure that where both sources contained the same samples, the data were identical. The data was analyzed via Positive Matrix Factorization using the PMF2 software of Paatero and Tapper.[17] Details of PMF analysis, including criteria for determining the 'correct' number of factors are provided in supporting information.

A major challenge of this analysis lay in the inconsistencies in the various data sets. PCBs were analyzed via EPA method 1668 using both of the gas chromatography columns allowed under this method (DB-5

and SPB-octyl). Because of their very different co-elution patterns, PCB data from these two columns was never combined in any of the data sets for PMF analysis. In general, water column (and, incidentally, biota) samples were sent to the contract lab that used the SPB-octyl column, while sediment samples and stormwater samples were sent to labs using the DB-5 column, although all labs received some of each type of sample. We note that this study design is not optimal and greatly complicates the data management, validation, and use. Generally it is advisable to use one GC column and common reporting formats for all samples in a given study.

A second major challenge in using this data was the absence of surrogate recoveries and sparse information about limits of detection (LOD), both of which are needed to construct accurate input matrices for PMF analysis. Where concentrations were below detection limit, the LOD was reported instead of the measured concentration in STORET but not in the RI database. Thus for the LOD matrixes for PMF analysis, the limited data on LODs were used to reconstruct what the LODs must have been for congeners that were detected, based on the assumption that LODs were the same for all congeners in a homologue in any given sample. In the concentration matrix, concentrations that were below detection limit were replaced with one-half of the inferred detection limit.

The uncertainty matrix is usually constructed from the relative standard deviation of the percent recoveries of the surrogate that is applied to each analyte. In the total absence of surrogate recovery information, the uncertainty matrix was borrowed from previous studies that used the same analytical methods and the same matrixes i.e. Du et al. [5] for the water column PCBs, Rodenburg et al.[10] for the water column PCDD/Fs, and Praipipat et al. [13] for the sediment PCBs.

Three data matrices were analyzed:

PCBs in sediment: PCBs in sediment were measured using the DB-5 (or equivalent) column, on which PCBs 4 and 10 co-elute. This is important because PCB 4 (2-2; numbers before the dash refer to the chlorine positions on ring 1, and the numbers after the dash refer to the chlorine positions on ring 2) is an indicator of microbial dechlorination.[2, 3, 9, 18] The final data matrix consisted of 83 peaks (116 congeners) in 401 sediment samples. Of these, 1.3% were below detection limit.

PCBs in water column: this data matrix consisted of PCBs measured separately in the dissolved and particle phases. We summed these two phases with non-detected values set to zero to provide 'whole water' measurements which were used in the data matrix. For congeners that were below detection limit in both phases, we used one-half the detection limit of the phase with the lower detection limit as

a proxy value in the concentration matrix. These samples were analyzed using the SPB-octyl column, on which PCB 4 is resolved from PCB 10. Once combined, 120 whole water samples were available for PMF analysis. The final data matrix contained 85 peaks (129 congeners) in 120 whole water samples, of which 1.1% were below detection limit.

PCBs and PCCD/Fs in water column: The 17 2,3,7,8-substituted PCDD/Fs were measured in 78 samples of filters only (dissolved phase was not analyzed for PCDD/Fs). This same approach was used in the CARP, based on the assumption that the dissolved-phase concentration of PCDD/Fs is negligible.[6, 11] PCBs were also measured in both phases of these 78 samples, and their whole-water concentrations were used in the combined concentration matrix. Twelve of the 17 PCDD/F congeners were above detection limit in the majority of samples. PCB congeners were chosen for this analysis that had the highest concentrations and were indicative of dechlorination processes (i.e. PCBs 4 and 19 (26-2)). Thus the final data matrix consisted of 12 PCDD/Fs and 65 PCB congeners in 78 samples, of which 1.8% were below detection limit.

RESULTS

Four factors were resolved from the matrix of PCBs in sediment (denoted Sed1 through Sed4). Five factors were resolved from the matrix of PCBs in the water column (denoted factors W1 through W5), and seven factors were resolved from the matrix of PCBs and PCDD/Fs in the water column (denoted factors WD1 through WD7). Each of the resolved factors was compared to the Aroclor congener patterns from Rushneck et al. [19] Because a DB-5 column was used for the sediment analysis, the coelution pattern was sufficiently different from the pattern observed by Rushneck et al. (who used an SPB octyl column) that some congeners had to be discarded in the comparison of the factor fingerprint with the Aroclor pattern. For this reason, the assignment of Aroclors to factors is less certain for the sediment data. Factors that did not resemble Aroclors are shown in figure 1. Factors that did resemble Aroclors are shown in supporting information figure S-3 through S-5.

PCBs in sediment

Concentrations of Σ_{209}PCBs in the sediment samples ranged from 0.0045 to 37,000 ng/g (dry weight). The 10th, 50th, and 90th percentile concentrations were 7.5, 51, and 660 ng/g, respectively. These are somewhat higher than those found in the Delaware River, where the 10th, 50th, and 90th percentile concentrations were 0.66, 11, and 138 ng/g,[13] and lower than in the NY/NY Harbor where concentrations were 71, 630, and 1300 ng/g, respectively.[11] The organic carbon content of the sediment of the Portland Harbor averaged ranged from 0.02% to 36%, with a median of 1.7%, similar to the Delaware River, where organic carbon fractions ranged from 0.03% to 7.8% with a median of 1.2%. In the NY/NJ Harbor, total volatile solids ranged from 0.4 to 14% with a median of 7.5%. It has been suggested [20] that total volatile solids divided by a conversion factor of 1.8 is equivalent to organic carbon. Thus the organic carbon fraction in the NY/NJ Harbor ranges from 0.2 to 7.8% with a median of 4.2%.

Of the four factors resolved from the data matrix on PCBs in sediment, three strongly resembled Aroclors and together comprised about 99% of the mass in the sediment (see supporting information figure S-3). Factor Sed1 resembled Aroclor 1248 (R^2 = 0.877) and comprised 42% of the mass in the data set. Factor Sed2 resembled Aroclor 1254 (R^2 = 0.973) and comprised 28% of the mass in the data set. Factor Sed4 resembled Aroclor 1260 (R^2 = 0.939) and comprised 29% of the mass in the data set. Factor Sed3 (Figure 1) contained a high proportion (3.0%) of PCB 11 and was reasonably well described as a 2:1 mixture of Aroclors 1260 and 1254 (R^2 = 0.85). Factor Sed3 only comprised 1.1% of the mass in the data set.

What is notable about the sediment data is the lack of any factor related to the dechlorination of PCBs by bacteria, despite PCBs 4+10, 19, 44, and 47, which are markers for microbial dechlorination, being included in the data matrix. This in stark contrast to the Upper Hudson River, where dechlorination of PCBs occurs in sediments, especially in the Thompson Island Pool, and the dechlorination products are still measurable in the water column of the Upper New York Harbor (about 0.5 to 2 ng/L, ~10% of total PCBs) nearly 300 km downstream.[6] Although dechlorination products were observed in the discharges to the Delaware River,[9] no dechlorination signal was observed in the sediment or water column there.[13]

PCBs in water column

ΣPCB concentrations in whole water samples from the Portland Harbor were lower than those in the Delaware River and NY/NJ Harbor. They ranged from 0.044 to 12 ng/L. The 10th percentile, median, and 90th percentile concentrations were 0.14, 0.33, and 0.93 ng/L. In comparison, the 10th percentile, median, and 90th percentile concentrations for the Delaware were 0.77, 2.7, and 5.9 ng/L and for the NY/NJ Harbor were 0.72, 7.2, and 26 ng/L, respectively.

Of the five factors resolved from the data matrix on PCBs in the water column, three resembled Aroclors (see supporting information figure S-4). Factor W1 resembled Aroclor 1242 (R^2 = 0.89), factor W3 resembled Aroclor 1254 (R^2 = 0.80) and factor W5 resembled Aroclor 1260 (R^2 = 0.99). These factors constituted 16%, 16%, and 41% of the mass in the data set, respectively. Thus collectively, relatively unweathered Aroclors comprise about 72% of the PCBs in the water column.

Factor W4 (Figure 1) was rich in PCB 11 (40% of total PCBs). PCB 11 is known to be present as an inadvertent by-product in pigments that are used in consumer goods such as printed paper and clothing, as well as paint.[21-25] Even when PCB 11 was removed, this factor did not resemble any of the Aroclors. Factor W4 constituted 6.3% of the mass in the water column under all flow regimes, but 16% of mass under stormwater influenced flow conditions, and only 3-6% under other flow regimes. In previous work, we surmised that the factor dominated by PCB 11 in the Delaware River [5] and NY/NJ Harbor [6] was related to stormwater, treated wastewater discharges, and combined sewer overflows, based on its prevalence during high flow events. Thus it appears that factor W4 is similarly related to stormwater and combined sewer overflows in Portland Harbor. PCB 11 concentrations ranged from 1.7 to 78 pg/L, with 10th, 50th, and 90th percentile concentrations of 5.3, 22, and 47 pg/L. In two samples, the PCB 11 concentration alone was greater than the 64 pg/L federal water quality standard for Σ_{209}PCBs. For comparison, in the NY/NJ Harbor, the median whole-water PCB 11 concentration was 62 pg/L and PCB 11 alone was above the federal water quality standard in 44% of all samples. New York State's water quality standard for Σ_{209}PCBs is just 1 pg/L (http://www.dec.ny.gov/regs/4590.html#16130). PCB 11 exceeded that level in 87% of all samples. In the Delaware River, the median whole-water PCB 11 concentration was 16 pg/L. It exceed the federal water quality standard in one sample out of 141. The local water quality standard for Σ_{209}PCBs in the Delaware River is 16 pg/L.[26] This was exceeded by PCB 11 alone in 47% of samples. This information adds to the growing body of evidence that PCB 11, which enters the environmental primarily through the use of various organic pigments, is a significant environmental concern.[21, 22]

Factor W2 (Figure 1) was dominated by PCB 4 (10% of total PCBs) and PCB 19 (15%), and contained reasonably high proportions of PCBs 44 (23-25)+47(24-24)+65 (2356) (9%) and PCBs 45(236-2)+51(24-26) (4%). All of these congeners are known to be markers of the dechlorination of PCBs by bacteria under anaerobic conditions.[2, 3, 9, 18] In the Delaware dischargers[9] and the NY/NJ Harbor dischargers[10], two dechlorination factors were observed. The 'advanced' dechlorination factor was dominated by PCBs 4 and 19 and was associated with combined sewers, groundwater, and landfills. In contrast, the 'partial' dechlorination factor was dominated by PCBs 44+47+65 and PCBs 45+51 and was most closely associated with separate sanitary sewers. We speculated [9] that this could be due to sulfidogenic conditions occurring in separate sewers, as opposed to methanogenic conditions which are more likely to prevail in combined sewers and groundwater. In contrast, only one dechlorination factor was observed in the water column of the NY/NJ Harbor.[6] Thus the absence of a partial dechlorination factor in Portland Harbor is perhaps not surprising, since any separate sewers in the region lead to the Columbia Boulevard Treatment Plant, which discharges into the Columbia River, not the Portland Harbor. A comparison of the congener patterns of the various dechlorination factors observed in the Portland Harbor water column, Delaware dischargers, NY/NJ Harbor dischargers, and NY/NJ Harbor water column is shown in supporting information, figure S-6.

Factor W2 comprised 22% of the mass of PCBs in the Portland Harbor water column data set. In comparison, concentrations of the equivalent dechlorination factor were around 17-42 ng/L (58-89% of the sum of PCBs) in the water column in the Upper Hudson River,[6] where extensive dechlorination of PCBs occurs in the sediments. In the Delaware River, about 19% of the PCBs in the effluents from point dischargers consisted of dechlorinated PCBs, but the dechlorination signal was not discernible in the water column. Thus the dechlorination of PCBs is more extensive in the Portland Harbor than in the Delaware River, but not as extensive as in the Hudson River.

Factor W2 contains only 0.1% PCB 11. The dechlorination factor in the Delaware River dischargers similarly contained virtually no PCB 11.[9] This suggests that PCB 11 is not an important product of the dechlorination of PCBs by bacteria. Also, it suggests that the dechlorination happening in the Portland Harbor is not closely associated with wastewater collection and treatment, since these types of sources would tend to contain PCB 11.

In the dechlorination signals from the NY/NJ Harbor water column[6] and Delaware River dischargers,[9] PCB 4 was more abundant than PCB 19. The ratio of PCB 4 to PCB 19 was 1.97 in the Delaware dischargers and 3.65 in the NY/NJ Harbor. In contrast, in Portland Harbor, PCB 19 was more abundant

that PCB 4 and the 4/19 ratio was 0.65. While a few strains of bacteria have been identified that can remove chlorines at the *ortho* positions,[27, 28] generally this is not observed in natural systems. According to the Aroclor compositions measured by Rushneck et al.,[19] if chlorines in the *ortho* position are not removed, the final 4/19 ratio would be greater than one for all Aroclors with 54% or less chlorine content (i.e. Aroclors 1016, 1242, 1248, and 1254). The only widely-used Aroclor that could produce a 4/19 ratio less than one is Aroclor 1260, which was the most abundant Aroclor in the PMF solution. This may indicate that in the Portland Harbor, 1260 is the main substrate for dechlorination, while in other systems such as the NY/NJ Harbor and Delaware River (where Aroclor 1260 was less abundant overall), Aroclors with lesser chlorine content were the main substrates for dechlorination.

PCBs and PCDD/Fs in water column

The combined data set containing both PCBs and PCDD/Fs was analyzed primarily to determine whether PCDD/Fs were also being dechlorinated. This approach was also used in previous work.[10] The results of the PMF analysis were not particularly useful for the apportionment of PCDDF and/or PCB sources because neither all of the major PCB congeners, nor all of the 17 PCDD/Fs were included in the data matrix. In addition, it is well known that compounds that have high concentrations in all samples, such as OCDD, are difficult to model via factor analysis.[29-31] Thus detailed presentation of the PMF results from the PCB+PCDDF data set can be found in supporting information figure S-5. Here the discussion is limited to factor WD3, which contains high proportions of PCB 4 (25%) and PCB 19 (37%) and thus represents dechlorination. Because OCDD typically dominates the concentrations of PCDD/Fs in the environment, it would be expected to be present in all of the WD factors.[29-31] In fact, in all of the other WD factors, the PCDDF portion is dominated by OCDD (at least 78% of Σ_{12}PCDDFs). In contrast, in factor WD3, OCDD is just 16% of the Σ_{12}PCDDFs and the factor is instead dominated by 1,2,3,4,6,7,8-HpCDD (73% of Σ_{12}PCDDFs). Other PCDD/F congeners that are abundant in factor WD3 were 1,2,3,4,6,7,8-HpCDF, 1,2,3,6,7,8-HxCDD and 1,2,3,4,7,8-HxCDF, all of which have been associated with microbial dechlorination in various studies.[31-33] In our previous report on the dechlorination of PCDD/Fs in sewers and landfills,[10] OCDD was similarly absent, 1,2,3,4,6,7,8-HpCDD was dominant, and 1,2,3,6,7,8-HxCDD and 1,2,3,4,7,8-HxCDF were abundant in the factor that contained high proportions of PCB dechlorination products. This pattern therefore appears to represent microbial dechlorination of PCDD/Fs. Because only the 2,3,7,8-substituted PCDD/Fs were measured in this data set, only the peri-dechlorination products were observed. As we observed in our previous work, [10] evidence that dechlorination occurs by this pathway in sewers suggests that the peri-lateral dechlorination pathway

may also occur in this system. In addition, dechlorination products with fewer than four chlorines may also be present, but were not measured in these samples.

Spatial and temporal variation in factors

The PMF results suggest that both PCDD/Fs and PCBs are dechlorinated in the Portland Harbor watershed, but that this dechlorination does not occur in the sediment. Where does it occur? The spatial variation in factor W2 concentration (Figure 2) is not consistent with a source upstream. Our previous work[9, 10] demonstrated that PCBs and PCDD/Fs can undergo extensive dechlorination in landfills, sewer systems (especially combined sewers), and groundwater. There are no landfills or treated sewage outfalls in the study area. Portland does have combined sewers with about 100 outfalls spread along the length of the Superfund site. However, as noted above, if the dechlorination signal were associated with wastewater, it would likely contain a higher fraction of PCB 11. Also, if CSOs were an important source of W2, the dechlorination signal would be relatively evenly distributed throughout the river and highest near clusters of CSO outfalls. Figure 2 demonstrates that this is not the case. During most sampling campaigns, the concentrations of factor W2 are highest around river mile 6.7, particularly on the east side of the river in an area known as Willamette Cove, where there are no CSO outfalls (see supporting information figure S-2 for a map of water sampling locations). Concentrations at this location are highest under low flow conditions, but are noticeably elevated even under high and stormwater influenced flow, suggesting that they are associated with groundwater inputs, not CSOs. In general, factor W2 was most abundant at low flow conditions (averaging 22% of total PCBs) versus just 9% under stormwater influenced flow and 4% under high flow conditions.

Willamette Cove is the site of an old shipbuilding/repair and drydock facility as well as a lumber mill, plywood mill, and barrel manufacturing site (http://www.deq.state.or.us/lq/ECSI/ecsidetail.asp?seqnbr=2066). This site is known to contain PCBs and PCDD/Fs in soils, groundwater and beach sand, and an oily sheen was noted on the groundwater and the surface water at this location during a visual inspection in 2011.

In the Delaware River, effluent from the former Philadelphia Naval Shipyard contained high levels of dechlorinated PCBs ranging from 0.28 to 8.4 ng/L (2% to 66% of total PCBs).[9] Like Willamette Cove, where Aroclor 1260 comprises an average of 51% of the sum of PCBs, the Philadelphia Naval Shipyard effluent also contained high proportions of Aroclor 1260 (between 8% and 72% of total PCBs). In

Willamette Cove (RM 6.7), concentrations of factors W2 (dechlorination) and W5 (Aroclor 1260) are strongly correlated (R^2 = 0.99, n = 9), in large part because these two factors comprise 64-100% of the PCBs in these samples.

There appears to be a second, less intense, source of PCB dechlorination products near river mile 8.5. This sampling location is within the Swan Island Basin, which is dominated by the Portland Shipyard. There are multiple CSO outfalls located within this Basin.

It is reasonable to conclude that groundwater discharge in the vicinity of the Willamette Cove is one of the main sources of dechlorinated PCBs (factor W2) to the Harbor. However, it is also plausible that dechlorination of PCBs and PCDD/Fs occurs in groundwater at several other locations and is discharged in smaller amounts throughout the Harbor. In the Delaware River, evidence for dechlorination of PCBs in groundwater was observed in the effluent from seventeen different sites, including seven of nine sites with known contaminated groundwater that had been listed under either the state remediation programs or the Superfund program.[9]

Groundwater flow into the Portland Harbor is extensive and rapid.[34] The hydrogeology of the Portland Harbor is characterized by three aquifers, all formed from alluvial sediments. The Harbor area is located downstream of a decline in gradient that has made it a depositional site since the early Pliocene.[35, 36] The resulting fine-grained sedimentary rocks became the Troutdale Formation where interbedded confining units created two confined aquifers.[36] During the Pleistocene, there was a braided channel in what later became harbor area, leaving deposits of interbedded gravels and sands of up to 50 meters thick. These deposits form an unconfined, unconsolidated aquifer where flow gradients are predominantly horizontal. Overlying this aquifer are silt, sand, and gravel derived from late-glacial Missoula floods.[37] Missoula floods deposits reach up to 300 feet thick and form the highly permeable uppermost unconfined aquifer.[36] The Willamette River has incised into these deposits in many places. Hydraulic conductivity in the upper, unconfined aquifer has a median value of 60 m per day with a high degree of variability depending on well location. Spring and seep discharge rates also vary with the rate of aquifer pumping, and a number of springs have reduced in discharge with population growth and an associated increase in the number of pumping wells. Median hydraulic conductivities are similar for the intermediary and Troutdale aquifers, ranging between 2-5 m per day.[38]

The connection between the upper, unconfined aquifer and the waters in Portland Harbor is maintained through seeps on the harbor bed, as most streams in the Portland Basin gain water from the aquifers

underlying channel beds.[38] The regional groundwater gradient drives discharge into the harbor, and seep flow from the aquifer to the harbor varies in rate with season and tide. The uppermost, unconfined aquifer has a strong connection to surface water, fluctuating in saturated thickness seasonally and with a diurnal tidal fluctuation of up to 1 m per day. Local permeability of the underlying aquifer and the hydraulic gradient between the aquifer and river stage drive the hydraulic conductivity and discharge rate from the aquifer to the overlying river and harbor waters. Thus it is reasonable to conclude that the major source of factor W2 is groundwater from one or more contaminated sites, while CSOs may also contribute. If correct, this conclusion suggests that controlling contaminant levels in groundwater flowing into the river will be crucial to reducing PCB and PCDD/Fs levels in Portland Harbor.

Implications

This investigation revealed that Portland Harbor, like the NY/NJ Harbor and the Delaware River, is impacted by PCB 11 generated inadvertently during production of organic pigments and dispersed throughout the environment by the use of such pigments in printed material, paints, etc.[21, 22, 24] Various data sources suggest that many other US waterways are impacted by PCBs from pigments, including the Santa Fe and Rio Grande Rivers in New Mexico (STORET), San Francisco Bay (California Environmental Data Exchange Network; http://www.ceden.org/), and the Houston Ship Canal (Houston, TX).[39]

In addition, investigations in three watersheds on both the east and west coasts of the US have now found evidence of microbial dechlorination of PCBs in compartments other than sediment, including groundwater, landfills, and sewers. The evidence is thus building that PCB dechlorination is much more common than previously assumed. In addition, evidence now suggests that PCDD/Fs are dechlorinated presumably by bacteria in sewers and landfills in the NY/NJ Harbor[10] and in groundwater in the Portland Harbor.

The accumulation of large data sets and access to those data sets via portals such as STORET has made these kinds of investigations possible. As data continues to accumulate, this type of data mining activity would be greatly aided by common methodology and reporting formats. The present analysis was hampered by inconsistencies in the PCB data that originate in a general lack of understanding about the specifics of the 1668 method and about the management of this kind of analytical data. Similar problems were encountered in the data from the CARP, where New York and New Jersey used two different columns for PCB analysis.[10] In the Delaware River, the Delaware River Basin Commission (DRBC) developed a set of modifications and instructions on the application of method 1668 that

allowed the accumulation of a homogeneous data set across sediment, water, and biota, with samples collected by over 100 dischargers and analyzed by at least 5 different contract labs, in a project overseen by three states and two EPA regions. These modifications are available at http://www.state.nj.us/drbc/quality/toxics/pcbs/monitoring.html. We suggest that the EPA and other organizations should prioritize better data management including the reporting of metadata such as detection limits and surrogate recoveries, and that all agencies should adopt DRBC's protocols for method 1668.

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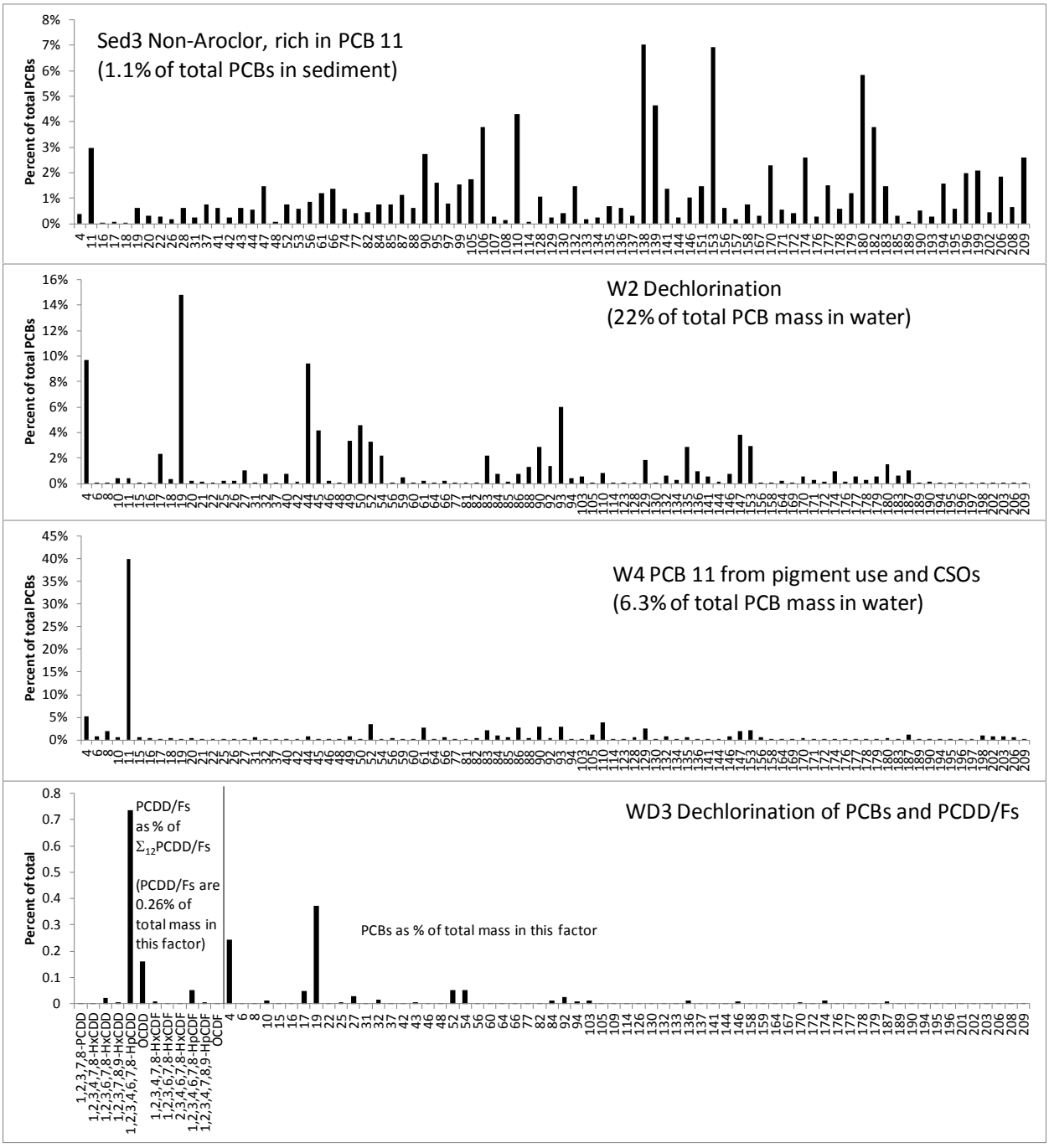

Figure 1. Selected fingerprints from factors derived from PMF analysis. Note that co-eluting congeners are labeled using the lowest IUPAC congener number. Complete information about co-elutions is provided in supporting information, Table S-1.

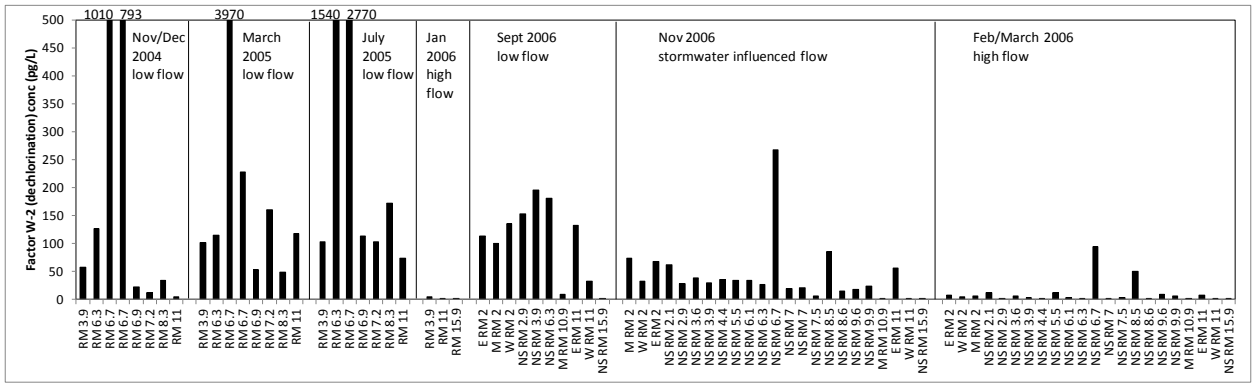

Figure 2. Concentrations of factor W2 (PCB dechlorination) in selected samples. Concentrations that are off scale are indicated above the bar. X-axis labels refer to river mile (RM) at which each sample was collected. E = east side of the river, M = middle, W = west. Unless NS (near surface) is indicated, all samples were vertically integrated. See supporting information figure S-2 for a map of sampling locations.